Indian Journal of Chemistry
Vol.36B, July 1997, pp.583 - 589

Kinetics and mechanism of the catalytic oxidation of cyclopentene to glutaraldehyde with aqueous hydrogen peroxide

Weilin Dai, Xiaojun Huang, Haiying Chen &Jingfa Deng*

Department of Chemistry, Fudan University, Shanghai 200 433, P.R. China

Received 21 August 1996; accepted 16 December 1996

Kinetics and mechanism of the catalytic oxidation of cyclopentene to glutaraldehyde by aqueous hydrogen peroxide have been studied. In tungstic acid-*t*-butanol system, cyclopentene is first oxidized to cyclopentene oxide almost quantitatively, which is then transferred into an intermediate. The intermediate, which is separated and identified as β-hydroxycyclopentylhydroperoxide, can easily change into glutaraldehyde during purification. The study shows that during the formation of the intermediate two by-products are also formed. These three reactions are found to be of first-order parallel reactions. The effects of temperature and concentration of tungstic acid, hydrogen peroxide, water and *t*-butanol on the reaction rates have been studied. A suitable mechanism for the reaction has been proposed.

Glutaraldehyde is a well-known compound which has been used widely[1,2]. It's utility has increased much, especially in recent years, because of its excellent bactericidal and sporicidal properties[3-5].

The traditional process[6] for the preparation of glutaraldehyde involves expensive raw materials and drastic reaction conditions. Therefore, many studies[7-9] have been performed to explore a new process for preparing glutaraldehyde using cyclopentene as a raw material since 1973. We have successfully developed a new method[10-12] which is now being used in industries for its high yield (70%) and moderate reaction conditions. The process involves hydrogenation of the raw material cyclopentadiene to cyclopentene which is then oxidized to glutaraldehyde using 30 or 50% aqueous solution of hydroperoxide as oxidant, tungstic acid as catalyst and *t*-butanal as solvent, and stirring the reaction mixture for 24 hr at room temperature. In this process, we find cyclopentene oxide (**A**) to be an intermediate and the conversion of cyclopentene to cyclopentene oxide to be almost quantitative. However, the conversion of cyclopentene oxide to glutaraldehyde is only about 70% and the side-products 1,2-cyclopentanediol (**C**) and 2-*t*-butoxylcyclopentanol (**D**)) are obtained in nearly 30% yield. Hence, a study of the mechanism for the conversion of cyclopentene to glutaraldehyde would be helpful from the industrial application point of view. Unfortunately, almost no attention has been paid to the use of hydrogen peroxide for the oxidative cleavage of epoxide to aldehydes. Frimer[13], who used MoO_5.HMPA to oxidize 3,4-dihydro-2*H*-pyran, developed a method for the synthesis of aldehydes from epoxides. But, because of the oxidant being very expensive, this method could not be used in industries. Although the conversion of cyclohexene to adipaldehyde has been reported by Payne[14], the main product in the reaction are cyclohexane-1,2-diol and 2-alkoxy-hexnol, and the yield of aldehyde is very low (about 10%), excluding the possibility of its application in industrial production. Though the possible mechanism has been proposed by Payne[14] and Frimer[13], it is still not widely accepted because no intermediates appearing in the mechanism has been isolated and characterised till now.

In this paper we report the kinetics and mechanism for the formation of glutaraldehyde from cyclopentene oxide and the detection of important intermediate, β-hydroxycyclopentyl hydroperoxide (**B**). The purpose of this study is to explore the optimum conditions for the preparation of glutaraldehyde and

to investigate a possible mechanism for the formation of aldehydes from epoxides using hydrogen peroxide as an oxidizing agent.

Materials and Methods

Instruments and reagents. The structure of the intermediate β-hydroxylcyclopentyl hydroperoxide (**B**) was determined by ^{1}H NMR (300MHz, MSL-300, $CDCl_3$, TMS), IR(Nicolet, FT-IR 5SDX, CaF_2, neat) and GC-MS(GC on a 8810 chromatograph, MS on a Finnigan MAT ITD 800 instrument).

Solvent (*t*-BuOH, AR), cyclopentene (Fluka) and 50% aqueous solutions of hydrogen peroxide were used without further purification. Following materials were prepared as authentic samples according to the methods described in literature: $WO_3.nH_2O$ (n =2-3)[15], cyclopentene oxide[16] and cyclopentane-1,2-diol[17]. Other authentic samples involved in the experiments were either purchased or prepared following the literature methods.

Preparation, purification and structure determination of β-hydroxylcyclopentyl hydroperoxide (B). In a 150 mL glass flask, 2mmol $WO_3.nH_2O$ was dissolved in 13 mL 50% aqueous solution of hydrogen peroxide at 40°C. The solvent (83 mL *t*-BuOH) and 10 mL cyclopentene were then added. The flask was equipped with a condenser and a magnetic stirrer. The reaction mixture was stirred at 35°C for 24 hr. In our previous work, the reaction mixture was decomposed at 60°C with 0.5% Pd / C to get the product (glutaraldehyde). In the present work, 1 mmol MnO_2 was added to the reaction mixture at room temperature to decompose free hydrogen peroxide (negative test with ammonium molybdate for free hydrogen peroxide[18]). The catalyst was filtered, the solvent distilled under reduced pressure and some water added to the residue to prevent polymerization. Salt was then added to the crude product (containing glutaraldehyde) and the solution shaken ether (3×30 mL). The ether extract was dried over magnesium sulfate and concentrated on a steam bath, taking care to hold the bath temperature below 50°C. An intermediate, characterized as β-hydroxylcyclopentyl hydroperoxide (**B**) was obtained from this concentrate by flash column chromatography over silica gel using ether as eluent. The structure of this peroxide was determined by ^{1}H NMR(300MHz), IR, GC-MS and other methods. The spectral data are — IR: 3300(vs, O-H), 2965(s, C-H), 2873(s, C-H), 1430(m), 1355(m), 1168(w, C-O), 1093(s, C-O), 1060(m), 1031(m), 956(s), 856 cm^{-1}(m, O- O); ^{1}H NMR : δ1.64-1.74(6H, m, 3×CH_2), 4.30(2H, m, Ha and Hb), 6.38(2H, s, OH and OOH); MS: m/z 119($[M+H]^+$, 6%), 101($[M-OH]^+$, 100), 100($[M-H_2O]^+$, 34), 85($[M-OOH]^+$, 64), 83($[M-OH-H_2O]^+$, 33).

Oxidation of cyclopentene oxide. In a 50 mL glass flask, $WO_3.nH_2O$ was dissolved in 50% aqueous solution of hydrogen peroxide at room temperature and then *t*-BuOH and cyclopentene oxide were added to it. The flask was equipped with a condenser and a magnetic stirrer. The reaction mixture was stirred at 35°C. The product was analyzed by GC.

Measurement of kinetics. $WO_3.nH_2O$ (1.12g) was dissolved with 14 mL 50% aqueous solution of hydrogen peroxide at 15°C, and *t*-butanol added to this solution to make up its volume to 100 mL. The resultant solution was kept at low temperature.

In a 50 mL glass flask, a desired volume of catalyst solution (mentioned above), 50% aqueous solution of hydrogen peroxide and *t*-butanol were added and then 2 mmol cyclopentene oxide was added. The flask was equipped with a condenser and a magnetic stirrer. The reaction mixture was stirred at the desired temperature. The temperature ranged from 0° to 40°C. The time of the addition of cyclopentene oxide was regarded as zero time. At suitable time internals aliquots were taken and analyzed for A,B,C, glutaraldehyde and D by GC.

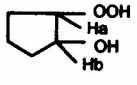
Product analysis. The reaction was monitored by 102- G gas chromatography. The products were detected on a flame-ion model GC using a 2 m column of SE-30 10% +PEG-20M 7% on white chromosorb 101. We found that compound **B** was easily changed into glutaraldehyde quantitatively under the temperature of detection. Hence, GC peaks of the two products were the same. To obtain separate concentrations of these two products, we can add KBH_4 as reductant to the sample to reduce **B** to **C** and glutaraldehyde to 1.5-pentandiol using *t*-butanol-water as solvent and boiling the mixture for five minutes. The concentration of glutaraldehyde will be easily obtained from the peak area of 1,5-pentandiol. In this way the concentration of **B** can be obtained too.

It is worth noting that during kinetic runs **B** is not changed into glutaraldehyde because of the lower concentration of tungstic acid. Hence, in these experiments the concentration of glutaraldehyde detected by GC expresses the concentration of **B**.

Results

Identification of the intermediate β-hydroxylcyclopentyl hydroperoxide (B). In a typical procedure for preparing glutaraldehyde, reported in our previous works, cyclopentene was oxidized with aqueous hydrogen peroxide for about 24 hr. After the oxidation, the reaction mixture was analyzed by GC at elevated temperature (150°C) and decomposed at 60°C with Pd / C to obtain glutaraldehyde. However, when MnO_2 was used, which can only decompose free H_2O_2 at room temperature[17], to decompose free hydrogen peroxide completely at the end of the oxidation, iodometric titration still indicated the presence of peroxide. This peroxide was separated by flash column chromatography over silica gel using ether as eluent.

The structure of the peroxide was determined by spectral techniques. In the ^1H NMR spectrum, a low flat singlet (δ 6.38) (Figure 1) that disappeared when D_2O was added indicated the presence of hydroxyl or hydroperoxyl group. The mass spectrum exhibited peaks at m/z 119 ($[M+H]^+$, $C_5H_{10}O_3$), 85 (C_5H_9O) and the base peak at 101 ($C_5H_9O_2$) (Figure 2), which suggested the presence of one hydroxyl and one hydroperoxyl group in **B**. The IR spectrum showed strong peaks at 3300 and 1093 cm^{-1} (Figure 3) indicating the presence of a secondary OH group. The structure **B** for the peroxide was verified by its reduction to cyclopentane-1,2-diol by KBH_4.



(B)

As mentioned in our previous paper, cyclopentene oxide was the initial product in the preparation of glutaraldehyde from cyclopentene with aqueous hydrogen peroxide catalyzed by tungstic acid. Thus, β-hydroxylcyclopentyl hydroperoxide was supposed to result from the oxidation of epoxide. Figure 4a shows a typical plot of cyclopentene oxide consump-

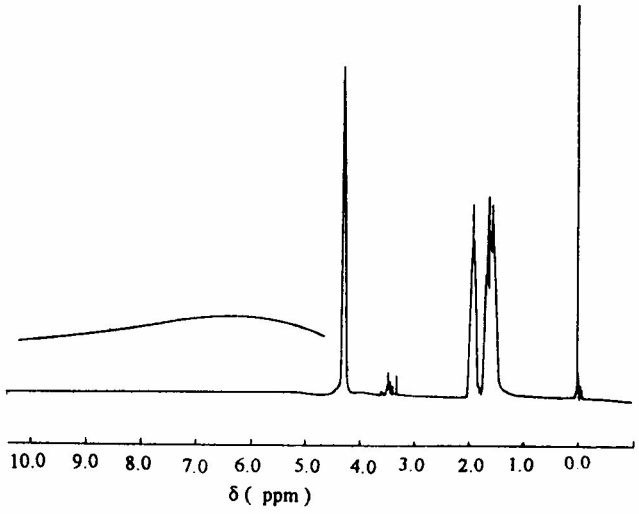


Fig. 1 — ^1H NMR spectrum of **B**

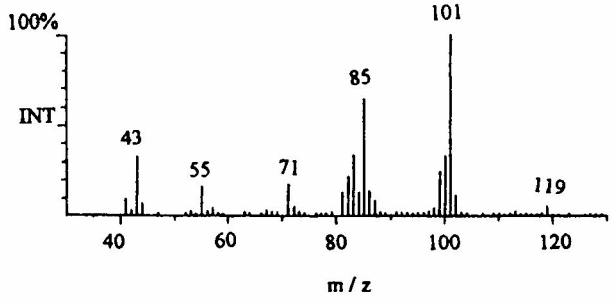


Fig. 2 — MS spectrum of **B**

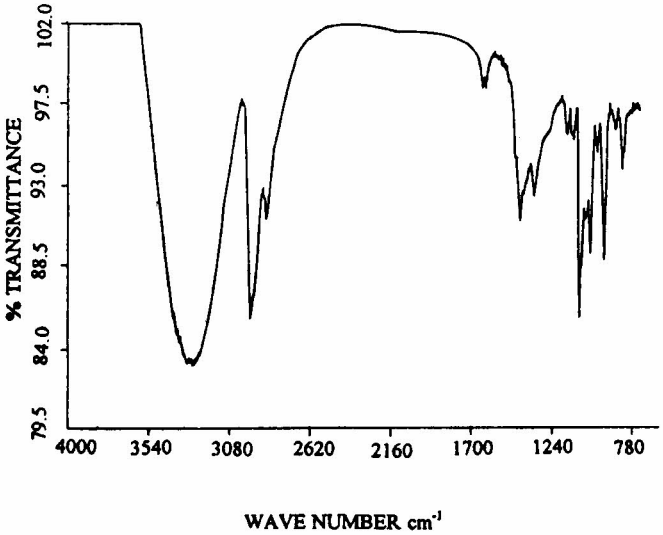


Fig. 3 — FT-IR spectrum of **B**

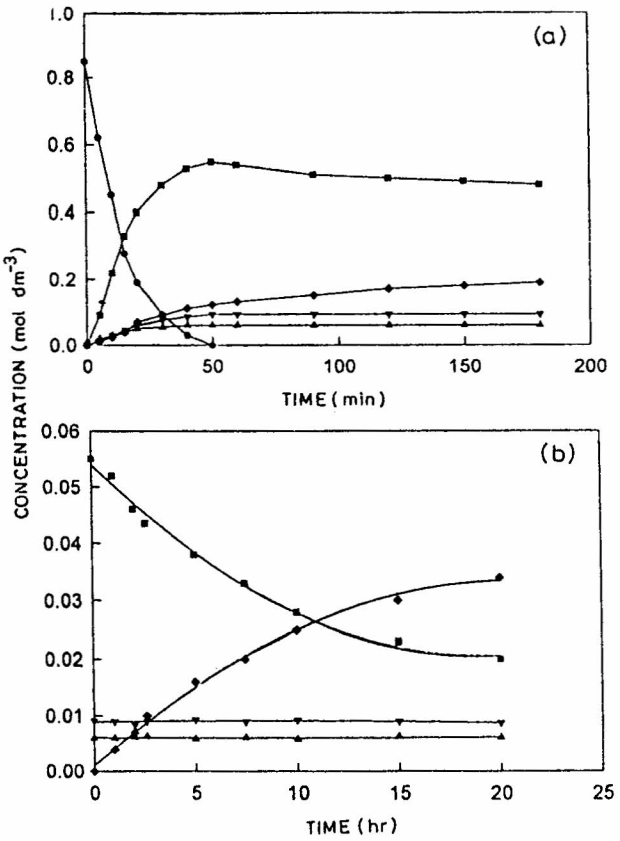
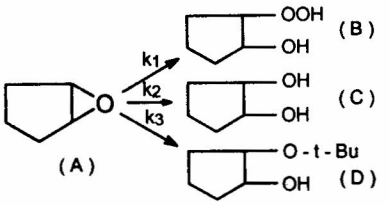


Fig. 4 — Oxidation of cyclopentene oxide (A) with hydrogen peroxide and $WO_3.nH_2O$ in *t*-BuOH at 35°C[Catalyst 0.2mmol, hydrogen peroxide(50%) 10.5mmol, *t*-BuOH 10 mL, amount of A in (a) 10 mmol and in (b) 1 mmol ■—B, ◆—glutaraldehyde, ▼—C, ▲—D, ●—A]

tion, β-hydroxylcyclopentyl hydroperoxide, cyclopentane-1,2-diol, 2-*t*-butoxyl-1-cyclopentanol and glutaraldehyde formation vs time at 35°C using $WO_3.nH_2O$ as catalyst and 50% aqueous solution of hydrogen peroxide as oxidant in *t*-butanol. At the end of the reaction, complete conversion of **A** was achieved with the formation of **B**, **C** and **D** while only small amount of glutaraldehyde was detected. Since **B** cannot result from **C** or/and **D**[11] under the same condition, it must result from the oxidation of **A**. The oxidation of **A** with higher ratio of $WO_3.nH_2O$ to **A** is shown in Figure 4b. It was noted that under this condition **A** was consumed completely as soon as the reaction was started by mixing, and **B**, **C** and **D** were detected with significant amount while no glutaraldehyde was detected at this moment. Thereafter, the concentration of glutaraldehyde increased with time and that of **B** decreased, while those of **C** and **D** remained the same. Therefore, it could be concluded that **B**, rather than **C** and **D**, was the intermediate from **A** to glutaraldehyde.

Kinetics of the formation of β-hydroxylcyclopentyl hydroperoxide (B). Cyclopentene oxide (**A**) can react with water and *t*-butanol, which are present in the reaction mixture, to form **C** and **D**, respectively. Therefore, together with the main reaction which resulted in **B** with H_2O_2, there are three parallel reactions in the system as shown in



Scheme I

Under a given condition in which $[H_2O_2]$, $[H_2O]$, [*t*-BuOH] >>[A], the relationship between [A], [B], [C], [D] and *t* was studied. The results showed that $\ln([A_o]/[A]) = k_o t$ (where k_o expresses the disappearance rate constant of **A**) and the ratio [B]:[C]:[D] was independent of time, indicating that this is a first-order parallel reaction. According to the principles of macroscopic kinetics, the relationship between concentration and time can be described by the following equations:

$$[B] = k_1/k_0[A]_0(1-e^{-k_0 t}) \quad ...(1)$$

$$[C] = k_2/k_0[A]_0(1-e^{-k_0 t}) \quad ...(2)$$

$$[D] = k_3/k_0[A]_0(1-e^{-k_0 t}) \quad ...(3)$$

where k_0, k_1, k_2 and k_3 can be obtained experimentally.

Under a typical reaction condition in which the mole fraction of tungstic acid (WOH) is 2.93×10^{-4}, H_2O_2 is 0.0751, H_2O is 0.172, *t*-BuOH is 0.740 and **A** is 0.0130, at t =35°C, the values of k_o, k_1, k_2 and k_3 were 1.94×10^{-4} s^{-1}, 8.92×10^{-5} s^{-1}, 6.53×10^{-5} s^{-1} and 3.65×10^{-5} s^{-1}, respectively. So [B]:[C]:[D]= 2.89:1:37:1. It is easy to see that $k_0 = k_1 + k_2 + k_3$, which agrees with the theoretical results obtained from the principles of macroscopic kinetics. Since the values of k_o, k_1, k_2 and k_3 will change with the mole fraction of WOH, H_2O_2, H_2O and the reaction

temperature, a set of experiments were designed to study the relationships between the rate constants and the mole fractions of the reactants or reaction temperature. Since *t*-butanol was used as solvent, its mole fraction can be treated as constant. Therefore, we did not study the mole fraction change of *t*-butanol with the rate constant.

(i)**The effect of concentration of tungstic acid**. The linear relationship between k_0 / X_{WOH}, k_1 / X_{WOH}, k_2, k_3 and the mole fraction of tungstic acid were experimentally found as:

$$k_0 = X_{WOH}(6.01 \times 10^2 X_{WOH} + 0.494)(r = 0.999) \quad ...(4)$$

$$k_1 = X_{WOH}(4.37 \times 10^2 X_{WOH} + 0.189)(r = 0.996) \quad ...(5)$$

$$k = 0.312 X_{WOH} - 3.00 \times 10^{-5} (r = 0.996) \quad ...(6)$$

$$k_3 = 0.160 X_{WOH} - 7.91 \times 10^{-6} (r = 0.997) \quad ...(7)$$

The relationships between k_0, k_1 and X_{WOH} are quadratic while those between k_2, k_3 and X_{WOH} are linear, suggesting that X_{WOH} exerted greater influence on k_1 than on k_2 and k_3. So a higher mole fraction of the catalyst would result in a higher yield of **B**, which in turn can be easily transferred into glutaraldehyde.

(ii) **The effect of concentration of H_2O_2 and H_2O**. The relationship between the mole fraction of H_2O_2, H_2O and the observed rate constant k_0 was found to be linear.

Similarly relationship between couples such as $X_{H_2O_2}$ and k_1, X_{H_2O} and k_2 was also found to be linear.

The linear relationships between k_0, k_1, k_2 and the mole fractions of H_2O_2 and H_2O were experimentally found as:

$$k_0 = 8.51 \times 10^{-4} X_{H_2O} + 3.36 \times 10^{-4} (r = 0.99) \quad ...(8)$$

$$k_0 = 1.32 \times 10^{-4} X_{H_2O} + 1.34 \times 10^{-4} (r = 0.999) \quad ...(9)$$

$$k_1 = 8.39 \times 10^{-4} X_{H_2O_2} + 3.25 \times 10^{-5} (r = 0.99) \quad ...(10)$$

$$k_2 = 3.20 \times 10^{-4} X_{H_2O} + 1\,28 \times 10^{-5} (r = 0.99) \quad ...(11)$$

These four equations are all linear equations. So a higher mole fraction of H_2O_2 and a lower one of H_2O will result in a higher yield of **B**. Table I shows the results:

(iii) **Effect of temperature**. The relationship between $1/T$ and $\ln k_0$, $\ln k_1$, $\ln k_2$, $\ln k_3$ was found to be linear. The linear equations were experimentally found as:

$$\ln k_0 = 17.09 - 7.719 \times 10^3 1/T (r = 0.999) \quad ...(12)$$

Table I — Effects of the mole fraction difference of WOH, H_2O_2 and H_2O on the yields of **B**, **C** and **D**

mole fraction	Yield(%)		
	B	**C**	**D**
		WOH(10^{-4})	
2.93	47.4	33.8	18.6
4.40	50.5	30.2	19.3
5.81	51.6	30.5	17.9
7.30	54.9	29.5	15.6
		H_2O_2	
0.0751	47.4	33.8	18.6
0.110	52.0	30.9	17.1
0.142	53.9	29.7	16.4
0.170	56.4	28.1	15.5
		H_2O	
0.172	47.4	33.8	18.6
0.231	46.2	35.7	18.1
0.290	44.6	37.9	17.5
0.333	43.4	39.6	17.0

Table II — Arrhenius constants (Ea and A_0) for the oxidation reactions

Reaction	Ea(kJ/mol)	A_0
Disappearance of **A**	64.0 ± 0.2	$(2.46 \pm 0.1) \times 10^7$
Formation of **B**	59.3 ± 0.2	$(2.02 \pm 0.1) \times 10^6$
Formation of **C**	68.9 ± 0.2	$(5.01 \pm 0.1) \times 10^7$
Formation of **D**	75.0 ± 0.2	$(3.20 \pm 0.1) \times 10^8$

Table III — Effects of temperature on the yields of **B**, **C** and **D**

T(°C)	Yield(%)		
	B	**C**	**D**
0	67.04	10.03	22.93
20	58.09	14.41	27.50
30	52.39	15.72	31.89
40	53.54	17.73	28.73

$$\ln k_1 = 14.61 - 7.155 \times 10^3 1/T (r = 0.999) \quad ....(13)$$

$$\ln k_2 = 17.82 - 8.315 \times 10^3 1/T (r = 0.998) \quad ...(14)$$

$$\ln k_3 = 19.66 - 9.048 \times 10^3 1/T (r = 0.999) \quad ...(15)$$

These linear equations indicated that the oxidation reactions mentioned above are in accordance with the Arrhenius equation, following which the values of Ea and A_0 could be obtained (cf. Table II).

In Table II, the increase in $Ea(Ea_1 < Ea_2 < Ea_3)$ suggested that a lower temperature should be employed to achieve a higher yield of **B** (cf. Table III). On the other hand, when the temperature went below 10°C, the oxidation reaction would become very slow. Hence, 25-35°C is a suitable range to keep a reasonable rate. This is also the reason why 35°C was adopted in the present method.

Discussion

The mechanism of formation of β-hydrocyclopentyl hydroperoxide (B) from cyclopentene oxide. On the basis of kinetics data obtained, a five-step mechanism was proposed as shown in Scheme II.

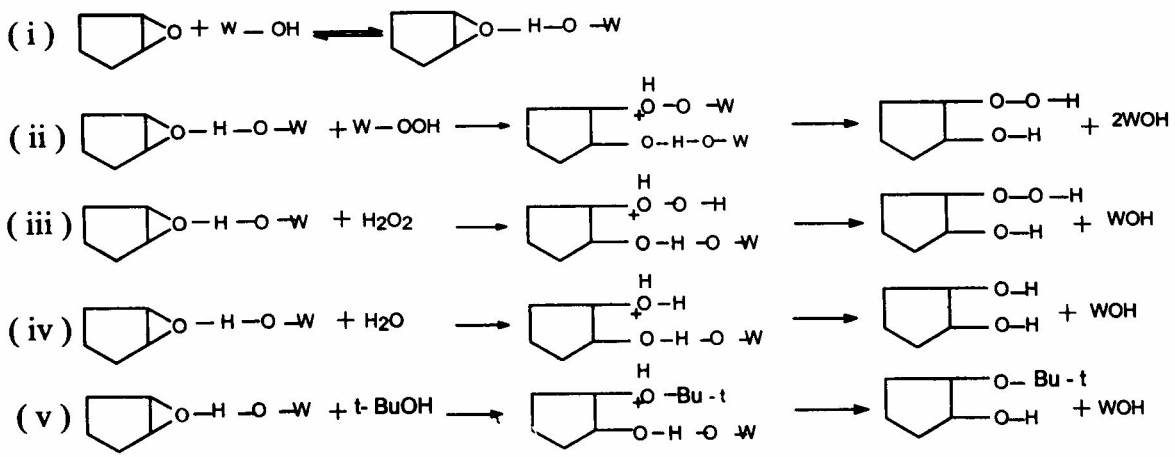
In Scheme II, the species WOOH is formed as: $WOH + H_2O_2 \rightarrow WOOH + H_2O$. In the present experiments we find that $X_{WOOH} = X_{WOH}$ and that X_{WOOH} does not change with the change in XH_2O_2.

The Mechanism of formation of glutaraldehyde from β- hydrocyclopentyl hydroperoxide (B). The organic peroxide **B** is stable, especially when dispersed in water. It will not change into glutaraldehyde if catalyzed by H^+. So the rearrangement will only occur under suitable condition using proper catalyst. Two procedures have been reported[9] for its rearrangement: heat-splitting and catalytic heat-splitting. For instance, if its solution was heated at 150°C for 1 hr, the yield of glutaraldehyde was 86%. The rearrangement temperature could be decreased if some noble metal catalysts such as Pd, Pt, Ir were present. In particular, the yield reached 92% when 5% Pd-C was added to the solution at 90°C. However, in the present study we found that if tungstic acid was used as catalyst **B** could be rearranged to glutaraldehyde at room temperature. Hence, W(VI) is a suitable catalyst for the rearrangement.

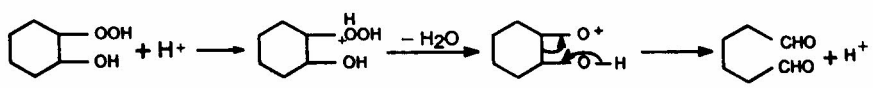
Payne[14], who used hydrogen peroxide to oxidize cyclohexene in a system similar to ours, suggested that adipaldehyde was formed from β-hydroxylcyclohexyl hydroperoxide (**B**) catalyzed by H^+ (cf. Scheme III).

This mechanism cannot be applied to our system because H^+ cannot catalyze the rearrangement of **B** as has been observed in our experiments. We therefore propose the mechanism as shown in Scheme IV.

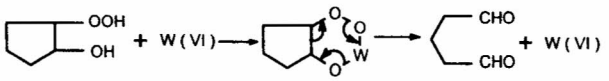
Frimer[13] suggested that the cleavage product 4-formyloxybutanal of 3,4-dihydro-2*H*-pyran was formed through an intermediate just like that proposed in our mechanism (see Scheme V)



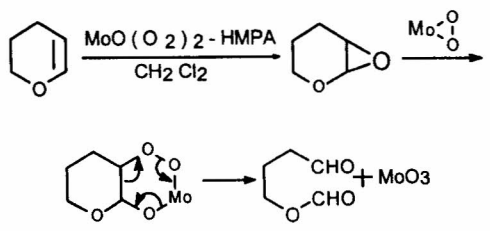
Scheme II



Scheme III



Scheme IV



Scheme V

Conclusions

(i) Two intermediates are found in the oxidation of cyclopentene to glutaraldehyde with aqueous hydrogen peroxide:cyclopentene oxide (**A**) and β-hydroxylcyclopentyl hydroperoxide (**B**).

(ii) In this catalytic reaction system, cyclopentene oxide can be changed into three products — β-hydroxylcyclopentyl hydroperoxide (**B**), cyclopentane-1,2-diol(**C**) and 2-*t*-butoxyl-1-cyclopentanol (**D**). These three parallel reactions are of first-order and follow Arrhenius equation.

(iii) Several methods are found to increase the yield of β-hydroxylcyclopentyl hydroperoxide (**B**), such as increasing the concentration of tungstic acid and hydrogen peroxide, decreasing the concentration of water and *t*-butanol or using lower reaction temperature.

References

1 Sabatini D, Bensch K & Barnett R, *J Cell Biol*, 17, **1963**, 19.

2 Fishman S N & Khodorov B I, *Biochim Biophys Acta*, 1, **1971**, 225.

3 Rubbo S D, Gardner J F & Webb R L, *J Appl Bacteriol*, 78, **1968**, 30.

4 Kuznetsova T A, Gareishina A Z & Limanov V E, *Neftepromysl Delo*, 1, **1980**, 32(Russ); *Chem Abstr*, 92, **1980**, 217683j.

5 Cater C W, *J Soc Leather Trades Chemists*, 47, **1963**, 259; 49, **1965**, 455.

6 Hess L G, Kurtz A N & Stanton D B, *Kirk-Othmer encyclopedia of chemical technology*, Vol.1, 3rd Edn, edited by H F Mark, D F Thmer, C G Overberger and G T Seaborg (John wiley & Sons, New York) **1978**, p.277.

7 (a) Helmut W, Wulf S & Wolfgan S *Ger Offen*, 2, 201, 456(1973); *Chem Abstr*, 79, **1973**, 91679c.

(b) Helmut W, Wulf S & Wolfgan S, *Ger Offen*, 2, 252, 674(1974); *Chem Abstr*, 81, **1974**, 25083q.

(c) Nippon Oil Co Ltd, *Jpn Kokai* JP 57,95,921[82,95,921]**(1982)**; *Chem Abstr*, 97, **1982**, 162366d.

(d) Hitoshi F, Teiji N, Hiroyuki I, Eiichiro I & Makoto M, *Chem Lett*, **1988**, 877.

8 Helmut W, Wulf S & Wolfgan S, *Ger Offen*, 2, 252, 719, **(1974)**; *Chem Abstr*, 81, **1974**, 25084r.

9 (a) Nippon Oil Co. Ltd, *Jpn Kokai Tokkyo*, JP 58, 121, 234[83,121,234] **(1983)**; *Chem Abstr*, 99, **1983**, 157834s.

(b) Hitoshi Y, Mitsuo M & Hirosuke I, *Eur Pat Appl EP*, 103, 099 (1984); *Chem Abstr*, 101, **1984**, 54614a.

10 Jiang A, Deng J, Xu X,, Chen H & Yan B, *Chinese Patent*, *CN*104445, 4**(1989)**; *Chem Abstr*, 116, **1992**, 6157s.

11 Deng J, Xu X, Chen H & Jiang A, *Tetrahedron*, 48, **1992**, 3503.

12 Xu X, Chen H, Deng J & Jiang A, *Acta Chimica Sinica*, 4, **1993**, 399.

13 Frimer A A, *J chem Soc Chem Comm*, **1977**, 205.

14 Payne G B & Smith G W, *J Org Chem*, 22, **1957**, 1682.

15 Jiang A, Pang Z & Jiang T, *Chinese Patent, CN*, 86 100321, 7 **(1986)**; *Chem Abstr*, 107, **1987**, 157613c.

16 *Org Synth Coll*, Vol.I, 185.

17 Owen L N, Smith P N, *J Chem Soc*, **1952**, 4026.

18 Chavanne G & Bode E, *J Am Chem Soc*, 52, **1930**, 1609.